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McMasterville, Québec J3G 1B6 (CA). **ZAGHIB, Karim** [CA/CA]; 3672 Belcourt, Longueuil, Québec J4M 2M7 (CA).

(21) International Application Number: **PCT/CA02/01888**

(74) Agent: **OGILVY RENAULT**; Suite 1600, 1981 McGill College Avenue, Montreal, Québec H3A 2Y3 (CA).

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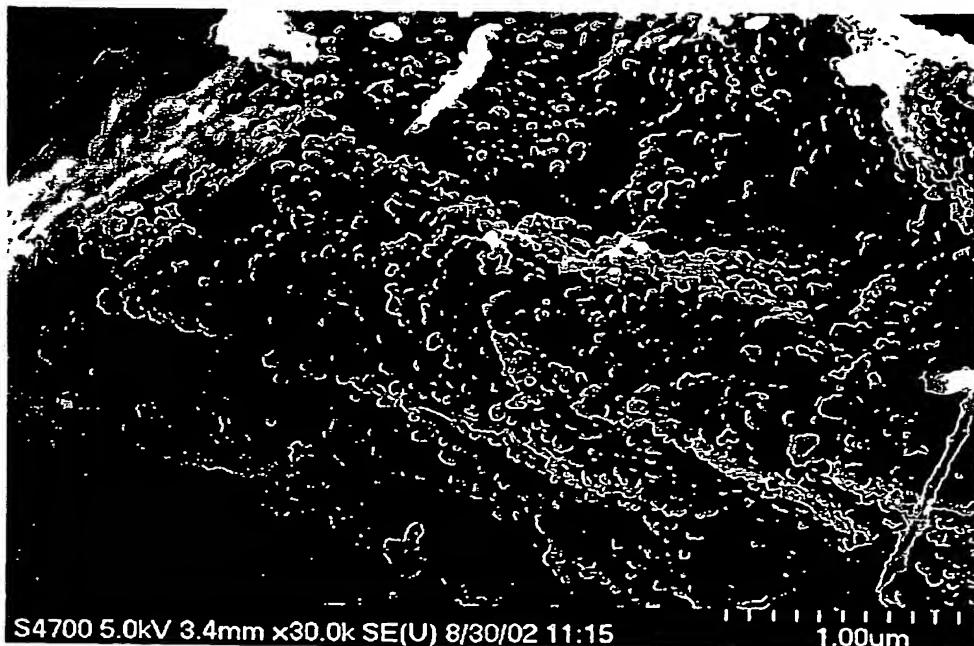
(71) Applicant (*for all designated States except US*): **HYDRO QUEBEC** [CA/CA]; 85, Ste-Catherine Street W., 10th floor, Montréal, Québec H2X 3P4 (CA).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **MALEKI, Hossein** [US/GE]; 179 Hampton Hallow Dr., 30043 Lawrenceville (GE). **SELMAN, Robert, J.** [US/US]; 5532 S. Shore no.12E, Chicago, IL 60637 (US). **GUERFI, Abdelbast** [CA/CA]; 8655 boul. Rivard, Brossard, Québec J4X 1W2 (CA). **DUPUIS, Élisabeth** [CA/CA]; 60B rue St-François,

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(54) Title: CARBON-CARBON COMPOSITE PARTICLES, THEIR PREPARATION AND USE THEREFORE AS NEGATIVE ELECTRODE FOR LI-ION BATTERIES



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(57) Abstract: A composite of particles of Carbon#1-Carbon#2, wherein Carbon#1 means a low crystallinity carbon and Carbon#2 means a high crystallinity carbon and the use of these particles in electrochemical systems, in sport equipments, in foundry industry and in the car and in aeronautic industries.

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**CARBON-CARBON COMPOSITE PARTICLES, THEIR PREPARATION  
AND USE THEREFORE AS NEGATIVE ELECTRODE FOR LI-ION  
BATTERIES**

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**TECHNICAL FIELD**

The present invention relates to composite carbone-carbone particles obtained  
10 from a low crystallinity carbon and of a high crystallinity carbon.

The present invention also relates to a process for preparing the composite carbon-  
carbon particles of the invention by dispersing and mixing together low  
crystallinity carbon particles with high crystallinity carbon particles.

15

The present invention also relates to a process for preparing the composite  
carbone-carbone particles of the invention by mixing carbon particles with a  
polymeric substance and by heating the mixture thereby obtained until  
carbonization of the polymeric substance on the surface of the carbon particles.

20

A further aspect of the present invention is the use of the composite particles inter  
alia in foundry industry, in sports equipment, in the automobile and in aeronautic  
industries and the use of those particles as constituents of electrode material in  
electrochemical systems.

25

**PRIOR ART**

Li-ion batteries are now considered one of the best existing power sources for  
portable electronics such as cell-phones, camcorders, laptop computer and power  
30 tools. A Li-ion cell typically consists of a carbon-based negative electrode (NE),  
porous polymer membrane separator (polypropylene and/or polyethylene) and a  
lithium transition metal oxide ( $\text{LiMO}_2$ , M=Co, Ni, or Mn) based positive electrode  
(PE), as described in Nishi in Advances in Lithium –ion batteries, edited by

W.Schalkwijk Cluwer Academic/plenum publishers, 2002, page 233, electrodes are made by casting slurries of active materials, polymer-based binder (i.e. polyvinylidene difluoride, PVDF) and small amounts of high surface area carbon onto metal foil current collectors. Mixtures of Li-salts and organic solvents provide an electrolyte medium for Li-ions to shuttle between the PE and NE. During charge, Li-ions deintercalate from the PE and intercalate into the NE, while the reverse takes place during discharge as mentioned in A. Webber and G. Blomgren in Adavances in Lithium -ion batteries, edited by W.Schalkwijk Cluwer Academic/plenum publishers, 2002, on page 185.

10

The evolving products require a Li-ion cell with a longer cycle-life, higher energy and charge/discharge rate capabilities. Long cycle-life e.g. is critical for the Li-ion battery to last the lifetime of the host device (such as: embedded electronics and medical prosthesis); and high capacity and rate capability are needed for the EV, aerospace and military applications.

15

For the development of Li-ions of such unique properties, battery manufacturers and research groups have been investigating possible applications of new and/or modified PE and NE materials.

20

These included utilization of In/Si-based intermetallic alloys, metal-carbon and carbon-carbon composites as NE-materials, and mixed metal-oxides as PE-material, as disclosed in R. Huggins in Handbook of battery materials edited by J. Besenhard Wiley-vch, 1999, page 359.

25

However, despite their high capacity, available NE-materials containing carbon-carbon composite, present the drawback of limited cyclic life, when available NE-materials containing In/Si-based intermetallic alloys despite their capacity present the drawback to be used commercial lithium-ion batteries.

30

Electrodes are made by casting slurries of active materials, polymer-based binder (i.e. polyvinylidene difluoride, PVDF) and small amounts of high surface area carbon onto metal foil current collectors. Mixtures of Li-salts and organic solvents provide an electrolyte medium for Li-ions to shuttle between the PE and

5 NE. During charge, Li-ions deintercalate from the PE and intercalate into the NE, while the reverse takes place during discharge.

The evolving products are demanding for Li-ion cells with longer cycle-life, higher energy and charge/discharge rate capabilities. Long cycle-life e.g. is

10 critical if the Li-ion battery should last the lifetime of the host device (such as: embedded electronics and medical prosthesis); and high capacity and rate capability are needed for the EV, aerospace and military applications.

For the development of Li-ions of such unique properties, battery manufacturers

15 and research groups have investigating possible application of new and/or modified PE and NE materials, including the utilization of In/Si-based intermetallic alloys, metal-carbon and carbon-carbon composites as NE-materials, and mixed metal-oxides as PE-material.

20 However, despite their high capacity, available NE-materials containing carbon-carbon composite present the drawback of cyclic life, when available NE-materials containing In/Si-based intermetallic alloys despite their capacity present the drawback to be used commercial lithium-ion batteries.

25 There was therefore a need for a positive electrode and/or negative electrode material free of the drawbacks usually associated with the corresponding prior art known materials and presenting inter alia at least one of the following properties: a long cycle life, a high capacity, a low self discharge, a good compatibility with a low volume expansion and with a low reactivity required for the safety of

30 batteries.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a graph that represents the thermal profile of the heat treatment of a  
(Carbon#1: polymerized PF-matrix) prepared according to a process of the  
5 invention as described thereafter under "sample preparation".

Figures 2a to 2d are schematic pictorial model representations of the steps  
occurring during processing of the proposed carbon-carbon composite material for  
NE in Li-ion cells, in the case wherein carbon#2 progressively covers carbon#1  
10 particles with a network of carbon#2.

Figure 3 A is an SEM image of the carbon-carbon material according to sample 1  
hereinafter defined in Table I, the carbon#2 is derived from carbonization of PF,  
which cover partially the surface of carbon#1 (graphite).

15

Figure 3B is the same SEM image as in Figure 3A, but at a larger scale.

Figure 4A is an SEM image of the carbon-carbon material according to sample 2  
defined hereinafter in Table I, the carbon#2 is derived from carbonization of PF  
20 and covers almost totally the surface of carbon#1 (graphite); the measured particle  
size of carbon#2 is from 39nm to 500nm.

Figure 4B is the same SEM image as in Figure 4A, at a larger scale.

25 Figure 5A is an SEM image of the carbon-carbon material according to sample 3  
as defined hereinafter in Table I. The carbon#2 is derived from carbonization of  
PF, which covers partially the surface of carbon#1 (graphite), but still some  
graphite particles are not covered at all. The particle size of carbon#2 is from  
20nm to 500nm.

30

Figure 5B is the same image as in Figure 5A but at a larger scale.

Figure 6A is an SEM image of the carbon-carbon material according to sample 4 as defined hereinafter in Table I. The carbon#2 is derived from carbonization of PF, which covers almost totally the surface of carbon#1 (graphite). The carbon#2 is more compact and it's particle size is from 20nm to 500nm.

Figure 6B is the same image as in Figure 6A but at a larger scale.

Figure 7 shows Transmission Electron Micrograph a carbon-carbon composite according to the invention, that has been prepared according to samples 3 and 4 and heat treated to 2.500 °C.

### DESCRIPTION OF THE INVENTION

A first object of the present invention is constituted by composite particles of carbon, thereafter named Carbon#1-Carbon#2 composite particles, wherein Carbon#1 means a low crystallinity carbon and Carbon#2 means a high crystallinity carbon.

In the framework of the present invention, the expression Carbon#1 means carbon particles, having a low crystallinity characterized by wide-angle X ray diffraction measurements, i.e by an average lattice constant  $d=(002)$  of 0.350 nm or more and a crystallite size  $L=(002)$  in the direction of C axis of 25 nm or less. Such low crystallinity carbon is more extensively described in Carbon electrochemical and physicochemical properties, John Wiley, New York, 1988.

According to a preferred embodiment of the invention low crystallinity carbons are selected in the group constituted by hard carbon, glassy carbons, polymer derived carbons and petroleum cokes.

In the framework of the present invention, the expression Carbon#2 means a high crystallinity carbon characterized by wide-angle X ray diffraction measurements, i.e by an average lattice constant  $d=(002)$  of 0.338 nm or less and a crystallinity size  $L=(002)$  in the direction of C axis of 40 nm or more. Such high crystallinity  
5 carbon is more extensively defined in Carbon electrochemical and physicochemical properties, John Wiley, New York, 1988. According to a preferred embodiment of the invention such high crystallinity carbon is selected in the group constituted by graphite, preferably natural graphites, kish graphite, pyrolytic graphite, gas-growth graphite or any artificial graphite.

10

A preferred family of Carbon#1-Carbon#2 composite particles of the invention is constituted by those composite particles having at least one of the following physical properties:

15

- a package density, according to the tap density method associated to the apparatus commercialized under the name Logan Instrument Corp. Model Tap-2, that is  $> 0,5$  g/cc.

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- a particle size, measured according to the SEM method associated with apparatus Microtac model X100 Particle Analyser, ranges from 0.5 to 100 micrometers; and

- a specific surface area, measured according to the BET method, ranging from 1 to 50  $m^2/g$ .

25

As shown inter alia in Figures 2, the composite particles of the invention may be described as low crystallinity particles of Carbon#1 embedded or surrounded by a matrix (or by a network) of graphite Carbon#2.

According to an another aspect of the invention, the composite particles of the invention may be described as particles of Carbon#2 embedded or surrounded by a matrix (or a network) of Carbon#1.

- 5 Therefore, particles of a high cristallinity carbon (preferably a graphitic carbon) are embedded within or surrounded by the matrix of a second carbon that has lower degree of cristallinity (graphitization), also known as hard carbon.

A second object of the present invention is constituted by the use of the composite  
10 particles according to the first object of the present invention as a constituent of an electrode material, preferably as a constituent of a N-E (negative electrode) material in electrochemical systems, in the foundry industry, in the car and in aeronautic industries, in sports equipment.

15 A third object of the present invention is constituted by negative electrodes comprising between 2 to 98 % and preferably by those comprising at least 90 weight per cent of a composite particles of the invention, the remaining being preferably constituted by at least one binder. The binder is preferably of the PVDF type.

20

A fourth object of the present invention is constituted by a battery system comprising at least one electrode containing carbon-carbon composite particles according the invention. Preferably, in the battery system of the invention, the electrode containing composite particles is a negative electrode.

25

According to an another embodiment, the battery system is of the N-E/electrolyte/PE type.

According to a further preferred embodiment of the invention the battery system consists of wined/stacked layers or of winded/stacked layers of electrodes of  
30 electrodes, at least one of said electrodes comprising carbon-carbon composite particles according to the invention.

A preferred embodiment is constituted by Li-ion battery comprising a negative electrode, a positive electrode and a porous polymer membrane separator for example of the Celguard type, wherein at least one of said electrodes is a negative  
5 electrode according to the invention.

A fifth object of the present invention is constituted by a process for preparing the composite material particles according to the first object of the invention. This process preferably comprises the steps of dispersing and mixing, preferably by  
10 using ball milling, at least one Carbon#1 powder, preferably in the form of a slurry of a polymeric substance that results in carbon particles by heat treatment. The polymeric substance, preferably a polymer with a high carbon content, is preferably dispersed in an organic solvent in a slurry that can easily stick on the surface of the carbon particles to be covered. The polymeric material is preferably  
15 dispersed in a liquid Phenolic Resin (PF). Appropriate phenolic resins are for example those commonly used in the foundry industry. Phenolic resins are the most widely used resin binders in the foundry industry. They are produced by polycondensation of phenols with formaldehyde. The three types of resins presented in the following Table differ in catalyst and mole ratio of reactants used  
20 in their preparation. Furthermore, they have different molecular structures and reactivities and require different curing agents.

Table - Some examples of Phenolic Resins

	Novolacs	Resoles	Polybenzylic ethers
ratio of phenol to formaldehyde	>1 acidic	<1 basic	<1 neutral, metal sal
pH conditions	thermoplastic	thermosetting	anhydrous
thermal behavior	shell process	hot-box process	thermosetting
foundry process		no-bake process	cold-box process
			no-bake process

There are two further categories of epoxy resins that may be successfully used,  
 5 namely the glycidyl epoxy, and non-glycidyl epoxy resins. The glycidyl epoxies are further classified as glycidyl-ether, glycidyl-ester and glycidyl-amine.

The diglycidyl ether of bisphenol-A (DGEBA) is a typical commercial epoxy resin and is synthesised by reacting bisphenol-A with epichlorohydrin in presence of a basic catalyst.

10 The Novolac Epoxy Resins are glycidyl ethers of phenolic novolac resins.

The mixing process is advantageously continued until complete dispersion of Carbon#1 in the PF and preferably until vaporization of 40 to 60 wt % of the containing solvent (preferably water, or organic solvent such as an alcohol) from  
 15 PF. Among preferred solvent for preparing the PF dispersions are water and organic solvents such as alcohols.

The heat treatment is preferably carried out at a temperature ranging from 400 to 2.800° Celsius, and more preferably at a temperature ranging from 1.000 to  
 20 2.500°C.

A sixth object of the present invention is constituted by a process for preparing a negative electrode. This process comprises the steps of:

- a) dispersing and mixing, preferably by using ball milling, at least one Carbon#1 powder, in preferably a liquid Phenolic Resin (PF), the mixing process being preferably continued until complete dispersion of carbon#1 in the PF and preferably until vaporization of 40 to 60 wt % of the containing solvent (preferably water, or organic solvent such as an alcohol) from the PF;
  - b) poring the mixture obtained in the preceding step on a support, preferably on a flat Al-plate, on a Cu-plate, on an alu-Exmet or on a cupfer Exmet, then heated preferably to 150-175 °C, more preferably to 160-170 °C and thermally soaked, for 1 to 5 hours, preferably for about 2.0 hours, the heating rate varying preferably from 3-8° C/min depending on the thickness of the sample;
  - c) after the preceding heating step, preferably converting the sample into solid sheets from which the support (AL-plate was separated); and
  - d) treating the Carbon#1: polymerized PF-matrix obtained in the preceding step at a temperature ranging from 600 to 2.500 °C, preferably at a temperature ranging from 600 to 1.000°C using 30-50° C/min heating rate following thermal profile shown in Figure 1. Then the carbon#2 is produced by carbonization of PF-matrix.

Any polymeric material, particularly any polymeric material with a high carbon content and more preferably any PF transforms to graphite up to heating through the following process:

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In the following examples, the PF material used was supplied in the year 2001 by  
30 Georgia Pacific Co., Lawrenceville, GA, in the United States of America under  
the reference Products # PF211.

- 1. PF Polymerizes to a rubbery gel on heating to 85°C (gelling process);

- 2. on heating to 120°C, the rubbery gel cures to form a hard cross-linked polymer by condensation reaction which produces water;

- 3. on heating to 225°C, the hard cross-linked polymer obtained in step 2 forms yellowish transparent material with lower density than its previous stages, this coincides with loss of more water and material having high porosity, at this stage neighboring carbon chains merge and start forming 3D-carbon matrixes;

- 4. on heating from 225°C to 500°C, the material obtained in the preceding step becomes free of water and yet contains appreciable amounts of hydrogen, this step is known as pre-carbonization carbonization step which was critical in controlling the porosity of the host material. Slower heating leads to smaller pore sizes;

- 5. on heating to 1000-1250°C, material volume shrinks, its electrical conductivity increases by many orders of magnitudes;

- 6. at temperatures above 1200°C, the material being depleted of hydrogen; and

- 7. further cross-linking and carbon chains start growing in 2D & 3D directions, this means that carbon#2 sticks on the surface of the carbon#1 particles and carbon #2 squeezes into itself when the temperature is increased to 2500°C.

Here, we are proposing the application of a new Carbon#1-Carbon#2 composite as N-E material for battery systems consisted of winded/stacked layers of electrodes with potential differences between them being dependant on their electrochemical properties. The other disclosing element of this proposal is the processing of the carbon-carbon composites noted above. The proposed material consists of carbon-carbon composite of 10-100  $\mu\text{m}$  particles.

This consisted of a highly graphitic carbon (e.g. graphite) embedded within or surrounded by the matrix of a second carbon that has a low degree of graphitization (known as hard carbons).

The low crystallinity carbon constituting of Carbon#1 has a sloppy voltage and a high medium voltage about 500 mV vs Li<sup>+</sup>/Li. This high sloppy voltage will be affected on the decreasing of the energy density of the batteries. However this is compatible with PC based electrolyte. This type of electrolyte is suitable for low temperature applications.

The high crystallinity carbon constituting of Carbon#2 has a flat voltage and low medium voltage about 100 mV vs Li<sup>+</sup>/Li. This low flat voltage will be affected on the increasing of the energy density of the batteries. However it is not compatible with PC based electrolyte.

## 25 EXAMPLES

The following examples are given for illustrative purpose only and may not be construed as constituting a limitation of the present invention.

### 30 Sample preparation:

The following steps were used to prepare the proposed material:

1- a Carbon#1 powder was dispersed in Liquid Phenolic Resin (PF) and the mixed using mixture ball milling. The mixing process was continued until complete dispersion of Carbon#1 in the PF and vaporization of 40 - 60 wt% of the containing alcohol from PF, both were assured.

5

2- the item-1 mixture was pored on flat Al-plate, then heated to 150-175°C and thermally soaked for 2.0 hours. The heating rate could vary from 3-8°C/min depending on the thickness of the sample, in our case heating of 5°C/min was used. After this heating process, the sample converts into solid sheets from which the AL-plate was separated.

10

3- item-3 (Carbon#1: polymerized PF-matrix) heat treated to 600 °C and then to 1000 or 2500°C using 30-50°C/min heating rate following thermal profile shown in Figure 1.

15

The PF matrix polymerizes and pre-carbonizes up to 450-475°C. During this step, PF generates water, which vaporizes while heating. This leads to increasing density and decreasing volume. Between 500-600 PF begins the early stages of carbonization steps, where the carbon graphite-sheets start buckling-up and building three-dimensional matrixes of randomly oriented short carbon layers with porous structure. PF porosity could depend on heat rate and thermal-soaking time in this temperature range. For longer heating time between 475-600°C, the PF pores size to become smaller. Above 600°C, the graphitization step starts and the graphite layer cross-link further. This process tends to squeeze the carbon#1 particles closer together and provides carbon-carbon composites with the low graphitized carbon matrix pressing over the highly graphitized carbon particles.

20  
25  
Figure 3 shows Transmission Electron Micrograph of the carbon-carbon composite heat treated to 2.500°C and as prepared according to samples 3 and 4.

30

The following Table 1 lists the data of carbon-carbon composite samples prepared for proof of the concept.

No.	Sample Description	Pore Area (m <sup>2</sup> / g)	Ave. Dia. (μ)	Bulk Density (g/cm <sup>3</sup> )	Skeletal Density
1	100g PF 50g-SFG-44 1000°C	9.184± 0.02	0.482	0.584	1.267
2	100g PF 40g-SFG-44/5%LiNO <sub>3</sub> 1000°C	13.198± 1	0.243	0.605	1.162
3	100g PF 70g-SFG-44 2500°C	3.198 ± 0.05	0.123	0.988	1.095
4	100g PF 70g-SFG-15 2500°C	6.550 ± 0.12	0.437	0.532	1.413

5

**TABLE I**

Carbon#1 is a carbon derived by heat treatment from 1.000 to 2.500 Celcius (preferably at 1.000 degrees Celcius) from phenolic resin.

10 Carbon#2 is an artificial graphite – commercialized under the name SFG 44 (particles having a size of 44 micrometers) and under the name SFG 15 (particles having a size of 15 micrometers by the Company Timcal (anciently Lonza in Swiss).

15 **Example 1**

In this example the carbon-carbon composite was made by mixing 100g PF with 50g of SFG-44 (artificial graphite) commercialized by Timcal (Swiss) and heated at 1.000°C for 2 hours in argon atmosphere. The SEM image of the carbon-carbon

material of the sample 1 is shown in Figure 1. The carbon#2 is derived from carbonization of PF, which cover partially the surface of carbon#1 (graphite). The electrochemical performance was obtained by using 1M LiClO<sub>4</sub> in EC-DMC as electrolyte. Three electrodes cell was used with lithium metal as counter electrode and reference. The reversible capacity of sample #1 is 218mAh/g at C/12 rate (charge and discharge in 12hours). The coulombic efficiency of the first cycle was 85%.

### Example 2

10 In this example the carbon-carbon composite was made by mixing 100g PF with 40g-SFG-44/5%LiNO<sub>3</sub> and heated at 1000°C for 2 hours in argon atmosphere. The SEM image of the carbon-carbon material of the sample 2 is shown in Figure 2. The carbon#2 is derived from carbonization of PF, which cover almost totally of 15 the surface of carbon#1 (graphite). The particle size of carbon#2 is from 39 nm to 500nm. The electrochemical performance was obtained by using 1M LiClO<sub>4</sub> in EC-DMC as electrolyte. Three electrodes cell was used with lithium metal as counter electrode and reference. The reversible capacity of sample #2 is 259 mAh/g at C/12 rate (charge and discharge in 12h). The coulombic efficiency of 20 the first cycle was 82%.

### Example 3

25 In this example the carbon-carbon composite was made by mixing 100g PF with 70g-SFG-15 and heated at 2500°C for 1 minute in argon atmosphere. The SEM image of the carbon-carbon material of the sample 3 is shown in figure 3. The carbon#2 is derived from carbonization of PF, which cover partially the surface of carbon#1 (graphite), but still some graphite particle not covered at all. The particle size of carbon#2 is from 20nm to 500nm.

30 The electrochemical performance was obtained by using 1M LiClO<sub>4</sub> in EC-DMC as electrolyte. Three electrodes cell was used with lithium metal as counter

electrode and reference. The reversible capacity of sample #3 is 235mAh/g at C/12 rate (charge and discharge in 12h). The coulombic efficiency of the first cycle was 45%.

5    **Example 4**

In this example the carbon-carbon composite was made by mixing 100g PF with 70g-SFG-15 and heated at 2500°C for 2 hours in argon atmosphere. The SEM image of the carbon-carbon material of the sample 3 is shown in Figure 4. The 10 carbon#2 is derived from carbonization of PF, which covers almost totally the surface of carbon#1 (graphite). The carbon#2 is more compact, it's particle size is from 20nm to 500nm.

The electrochemical performance was obtained by using 1M LiClO<sub>4</sub> in EC-15 DMC as electrolyte. A three electrodes cell was used with lithium metal as counter electrode and reference. The reversible capacity of sample #4 is 280mAh/g at C/12 rate (charge and discharge in 12h). The coulombic efficiency of the first cycle was 56%.

20 Among the improved properties of the new carbon-carbon material of the present invention over the known materials and particularly over the known NE materials are inter alia:

- the compatibility with propylene carbonate (PC);
- 25 - the low volume expansion;
- the high electrode density; and
- the low reactivity (safety).

It is to be understood that, while the foregoing invention has been described in 30 detail by way of illustration and example, numerous modifications, substitutions,

and alterations are possible without departing from the spirit and scope of the invention as described in the following claims.

**Claims:**

1. A composite of particles of Carbon#1-Carbon#2, wherein Carbon#1 means a low crystallinity carbon and Carbon#2 means a high crystallinity carbon.

5

2. A composite of particles of Carbon#1-Carbon#2 according to claim 1, wherein the Carbon#1 has, as measured by a wide-angle X ray diffraction, a low crystallinity characterized by an average lattice constant  $d=(002)$  of 0.350 nm or more and a crystallite size  $L=(002)$  in the direction of C axis of 25 nm or less.

10

3. A composite of particles according to claim 1 or 2, wherein the low crystallinity carbon is selected in the group constituted by glassy carbon, polymer derived carbons and petroleum coke.

15

4. A composite of particles according to claim 1 or 2, wherein the Carbon#2 has a high crystallinity as measured by a wide-angle X ray diffraction, an average lattice constant  $d=(002)$  of 0.338 nm or less and a crystallinity size  $L=(002)$  in the direction of C axis of 40 nm or more.

20

5. A composite of particles according to claim 4, wherein the high crystallinity carbon is selected in the group constituted by graphite, preferably natural graphites, kish graphite, pyrolytic graphite, gas-growth graphite and any artificial graphite.

25

6. A composite of particles of Carbon#1-Carbon#2 according to any one of claims 1 to 5, wherein the package density of said particles, measured according to the tap density method associated to the apparatus commercialized under the name Logan Instrument Corp. Model Tap-2, is superior or equal to 0,5 g/cc.

30

7. A composite of particles of Carbon#1-Carbon#2 according to any one of claims 1 to 4, wherein the particle size of said particles, measured according to the SEM method, associated to the apparatus Microtrac model X100 Particle Analyser, ranges from 0.5 to 100 micrometers.
- 5
8. A composite of particles of Carbon#1-Carbon#2 according to anyone of claims 1 to 7, having according to the BET method, a specific surface area ranging from 1 to 50 m<sup>2</sup>/g.
- 10 9. A composite of particles according to any one of claims 1 to 8, wherein the Carbone#1 is at least partially, preferably for at least 50 %, and more preferably for at least 70 % of its external surface, embedded or surrounded by a matrix of Carbon#2.
- 15 10. A composite of particle according to any one of claims 1 to 8, wherein the Carbone#2 is partially, preferably for at least 50 %, and more preferably for at least 70 % of its external surface embedded or surrounded by a matrix of Carbon#1.
- 20 11. A composite of particles of a high crystallinity carbon (preferably a graphitic carbon) embedded within or surrounded by the matrix of a second carbon that has a lower degree of crystallinity (preferably a graphitized carbon, also known as hard carbons).
- 25 12. A composite of particles according to anyone of claims 1 to 11, having a size measured according to the SEM (Scanning Electron Microscopy) method ranging from 1 to 50 micrometers, preferably the size of said particles ranges from 12 to 20 micrometers.
- 30 13. A composite of particles of high crystallinity carbon having a particle size ranging from 1 to 50 micrometers, said high crystallinity carbon particles

being at least partially covered by particles of low crystallinity having a particle size ranging from 10 to 500 nm, said low crystallinity carbon particles being attached to the surface of said high crystallinity carbon particle.

5

14. A composite of particles according to claim 13, wherein the size of the high crystallinity carbon particles ranges from 1 to 50  $\mu\text{m}$ , and is preferably from 5  $\mu\text{m}$  to 20  $\mu\text{m}$ .

10

15. A composite of particles of low crystallinity carbon having a particle size ranging from 1 to 50 micrometers, said low crystallinity carbon particles being at least partially covered by high crystallinity carbon particles having a particle size ranging from 1 to 50 micrometers, said low crystallinity carbon particles being attached to the surface of said high crystallinity carbon particle.

15

16. A composite of particles according to claim 15, wherein the size of the low crystallinity carbon particles ranges from 1  $\mu\text{m}$  to 50  $\mu\text{m}$ , and preferably ranges from about 5  $\mu\text{m}$  to about 20  $\mu\text{m}$ .

20

17. Use of particles according to any one of claims 1 to 16 in electrochemical systems, in sport equipments, in foundry industry, in the car and in aeronautic industries, and as a constituent of electrode material, preferably as constituent of negative electrode (N-E) material.

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18. A negative electrode comprising between 2 to 98 %, preferably comprising at least 90 weight per cent, of a composite material according to any one of claims 1 to 16, the remaining being preferably constituted by at least one binder, said binder being preferably of the PVDF type.

30

19. A battery system comprising at least one electrode containing composite particles according to anyone of claims 1 to 16.
- 5 20. A battery system according to claim 19, wherein the electrode containing composite particles is a negative electrode.
- 10 21. A battery system according to claim 19 or 20 of the N-E/electrolyte/PE type.
- 15 22. A battery system according to anyone of claims 19 to 21, wherein said batteries system consists of wined/stacked layers of electrode.
23. Li-ion battery comprising a negative electrode, a positive electrode and a porous polymer membrane separator, for example of the Celgard type, wherein at least one of said electrodes is an electrode according to claim 18.
- 20 24. A process for preparing the carbone-carbone composite material particles according to any one of claims 1 to 16, which process comprising the steps of dispersing and mixing at least one Carbon#1 powder, in a polymeric substance that results in carbon particles by heat treatment , preferably by heating for 5 minutes to 12 hours, at a temperature ranging preferably from 400 to 2.800° C, more preferably the temperature ranges from 1.000 to 2.500 °C, said polymeric substance being preferably dispersed in a solvent.
- 25 25. A process according to claim 24, wherein the dispersing step is carried out by using ball milling.
- 30 26. A process according to claim 24 or 25, wherein the polymeric substance is a liquid Phenolic Resin (PF).

27. A process according to anyone of claims 24 to 26, wherein the mixing process is continued until complete dispersion of Carbon#1 in the polymeric substance.

5 28. A process according to anyone of claims 24 to 27, wherein the mixing process is continued until vaporization of 40 to 60 wt % of the containing solvent from the polymeric substance.

10 29. A process according to anyone of claims 24 to 28, wherein the solvent is selected in the group constituted by water, or organic solvents such as an alcohol.

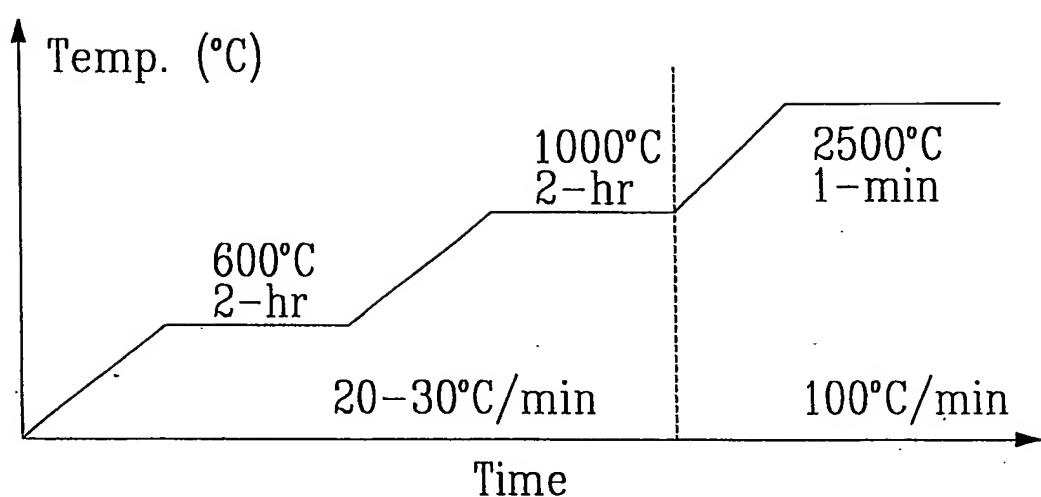
15 30. A process for preparing a negative electrode according to claim 18 comprising the steps;

- 15 a) dispersing and mixing, at least one Carbon#1 powder, with a polymeric material that may be converted in carbon particles by heat treatment;
- 20 b) putting the mixture obtained in the preceding step on a support, then heating said support covered by said mixture and then preferably thermally soaked;
- 25 c) after the preceding heating step, alternatively converting the sample thereby obtained into solid sheets from which the support is separated; and
- 30 d) treating the Carbon#1: polymerized polymeric material-matrix formed in the preceding steps b) or c) on the support, by temperature.

31. A process according to claim 30, wherein in step a) dispersing and mixing are carried out by ball milling.
- 5       32. A process according to claim 30 or 31, wherein in step a) the polymeric material is a polymeric material with a high carbon content, said polymeric material being preferably selected in the group constituted by liquid Phenolic Resins (PF), solubilized polysaccharides and mixture thereof.
- 10      33. A process according to claim 32, wherein in step a) the dispersion of carbon#1 is continued until vaporization of 40 to 60% of the solvent used to liquefying or for solubilizing the polysaccharide.
- 15      34. A process according to anyone of claims 30 to 33, wherein in step b) the support is heated to 150 to 175° C, more preferably to 160 to 170 °C.
- 20      35. A process according to claim 34, wherein in step b), the support is soaked for 1 to 5 hours, preferably for about 2.0.
- 25      36. A process according to claim 34 or 35, wherein the heating rate varies from 3 to 8° Celcius by minute, depending on the thickness of the sample.
- 30      37. A process according to anyone of claims 30 to 36, wherein in step d) the temperature ranges from 400 to 2.800 °C, preferably the temperature ranges from 600 to 2.500°C.
38. A process according to claim 37, wherein the heating is carried out at a rate , ranging from 30 to 50° C/min, preferably the heating rate follows the thermal profile shown in Figure 1.
- 30      39. A process according to claim 32, wherein the liquid Phenolic Resin is selected in the group consisting of novolacs, resoles and polybenzyllic ethers.

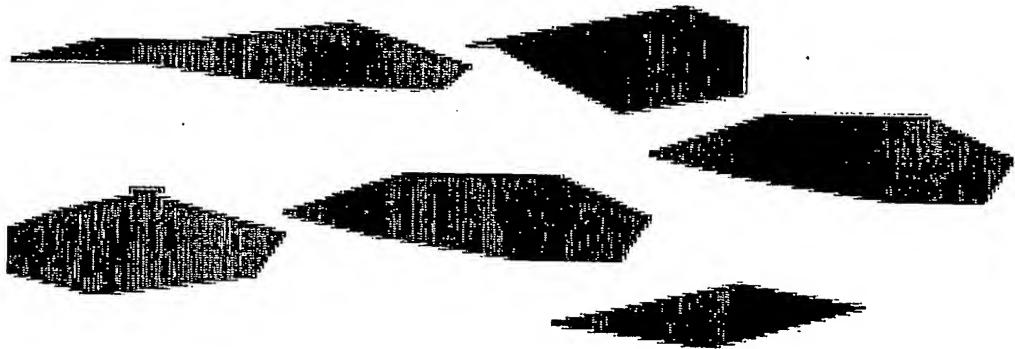
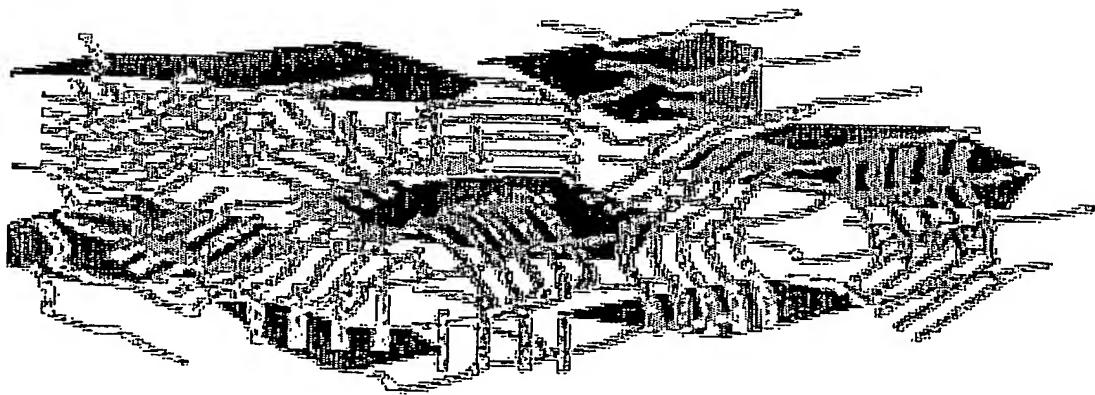
40. A process according to claim 32, wherein the polysaccharide is selected in the group constituted by gelatinized starches.
- 5     41. A process according to claim 39 or 40 wherein the liquid Phenolic Resin or the gelatinized starch is in the form of a slurry that presents a good applicability and a good adhesion on the support constituted by carbon#1 particles.

1/8



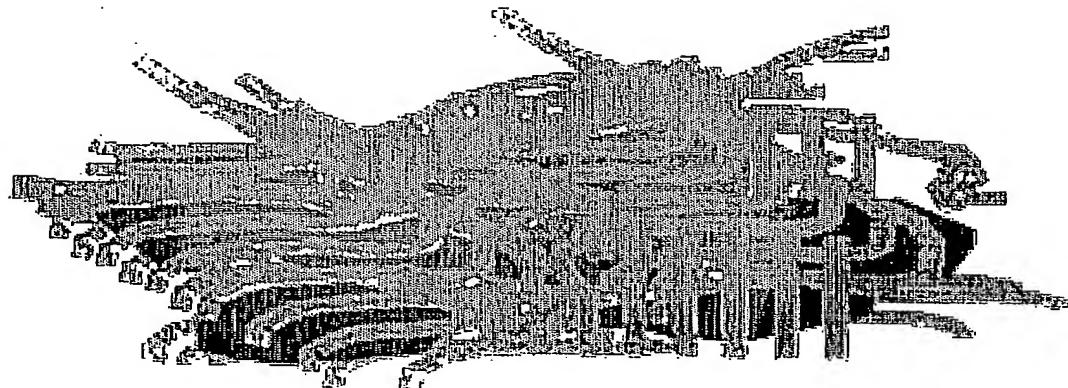
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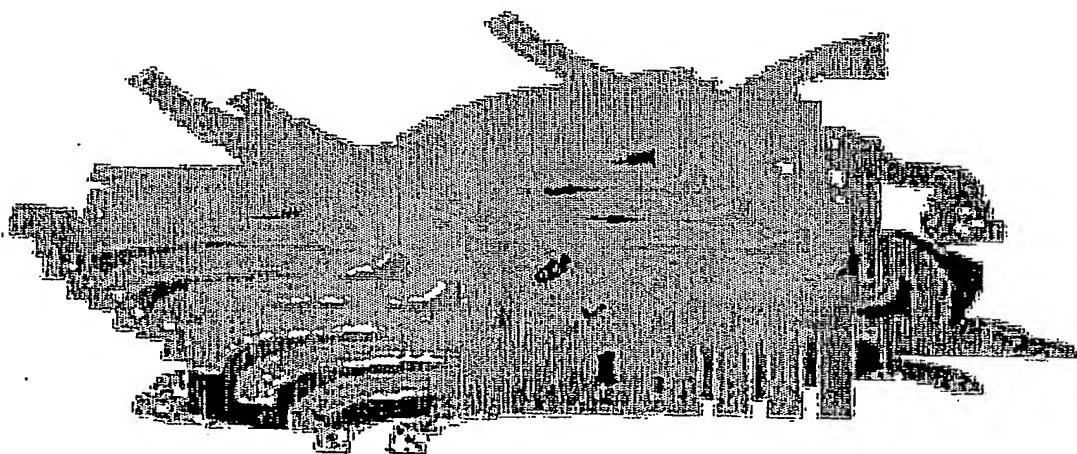
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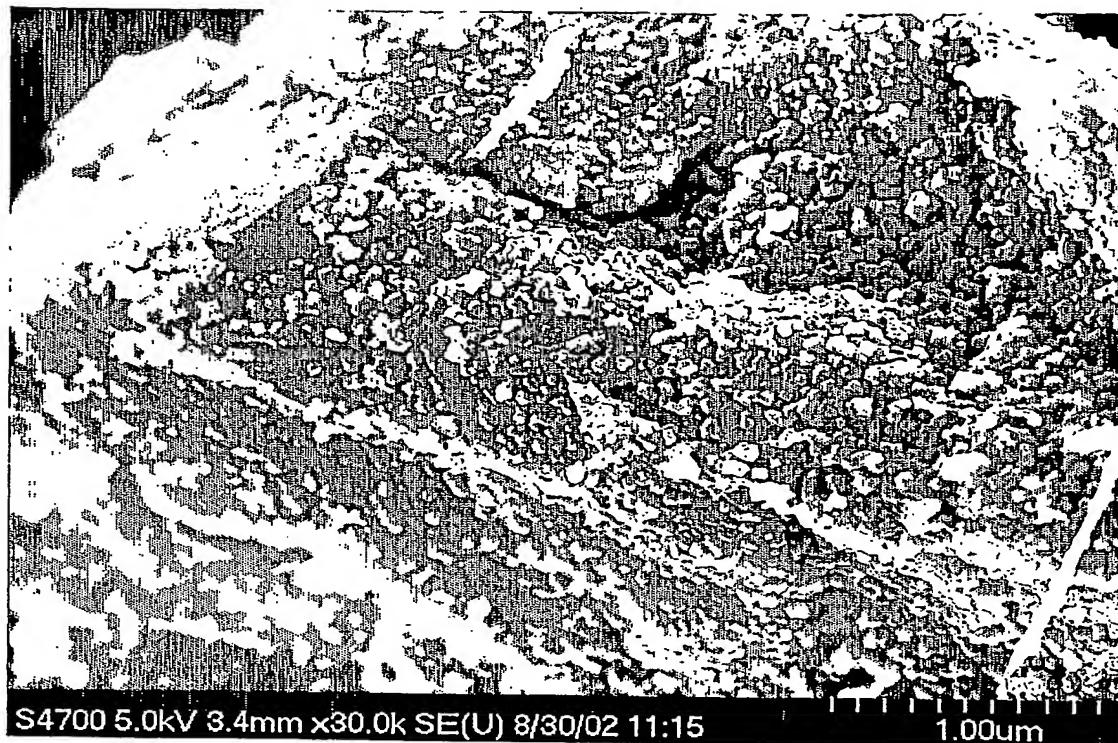
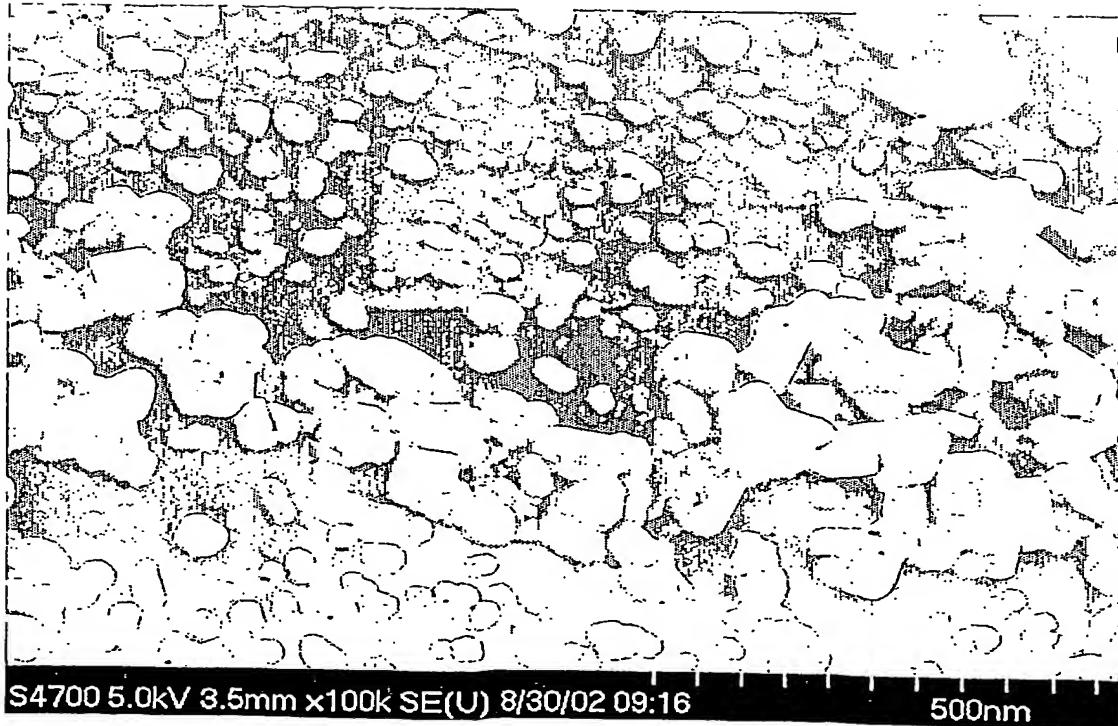
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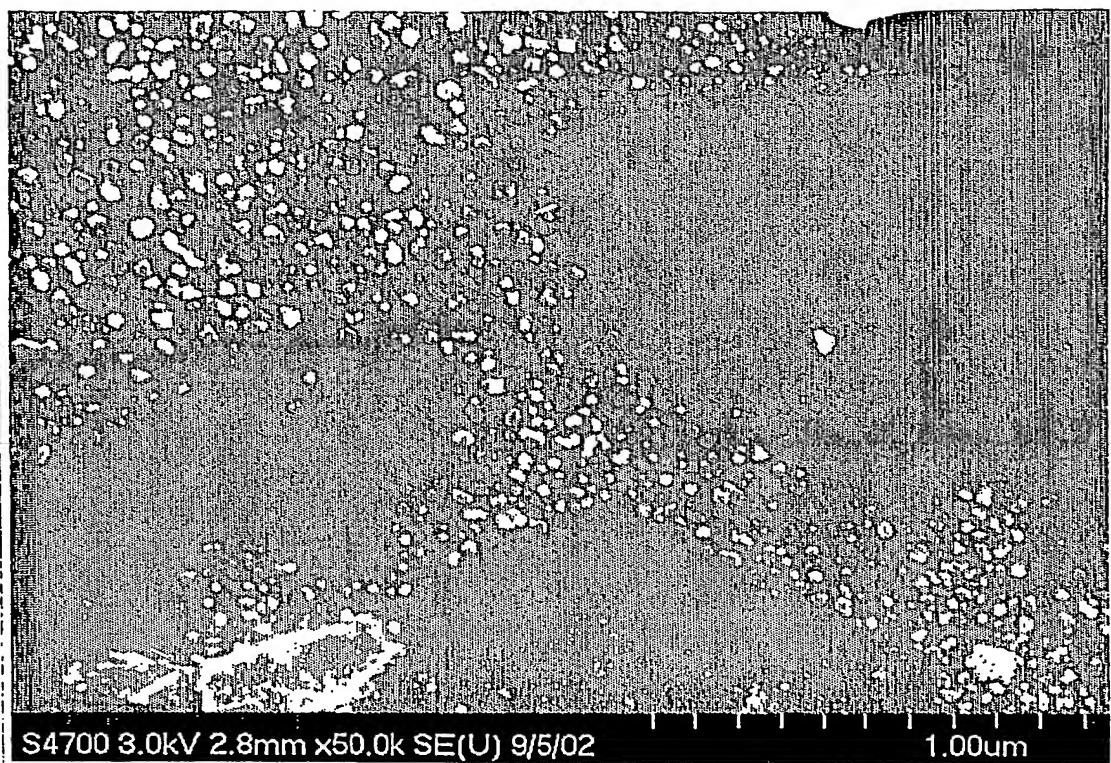
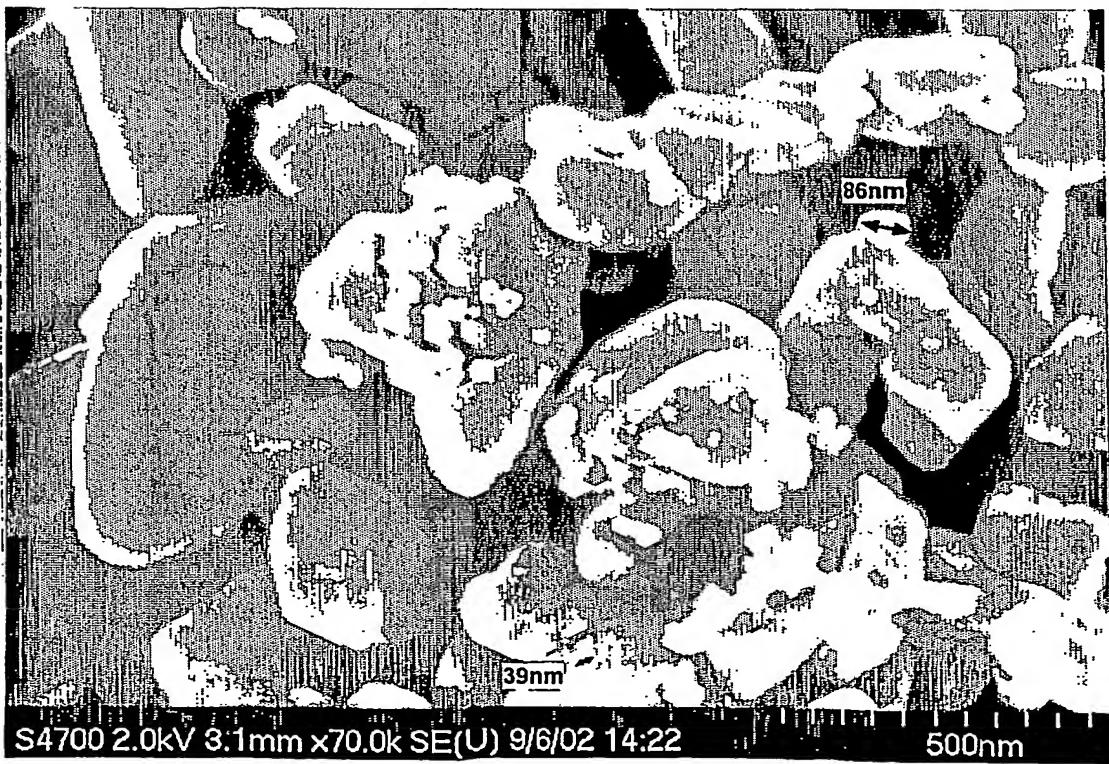
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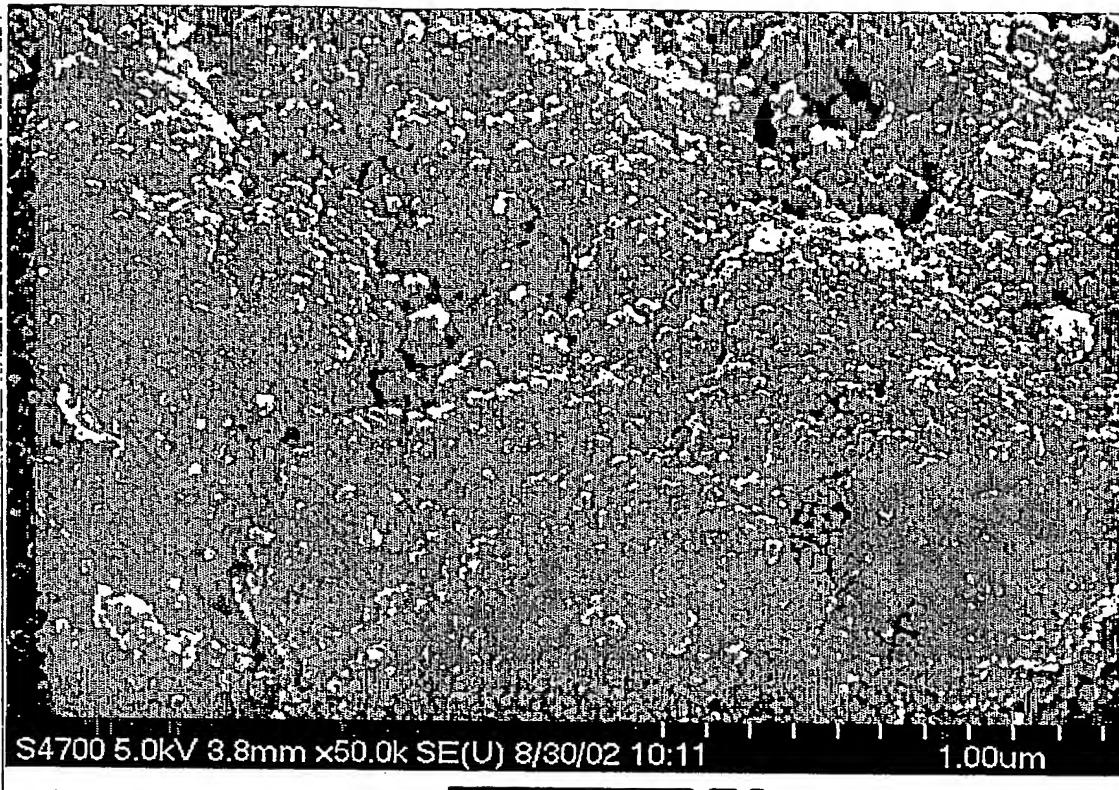
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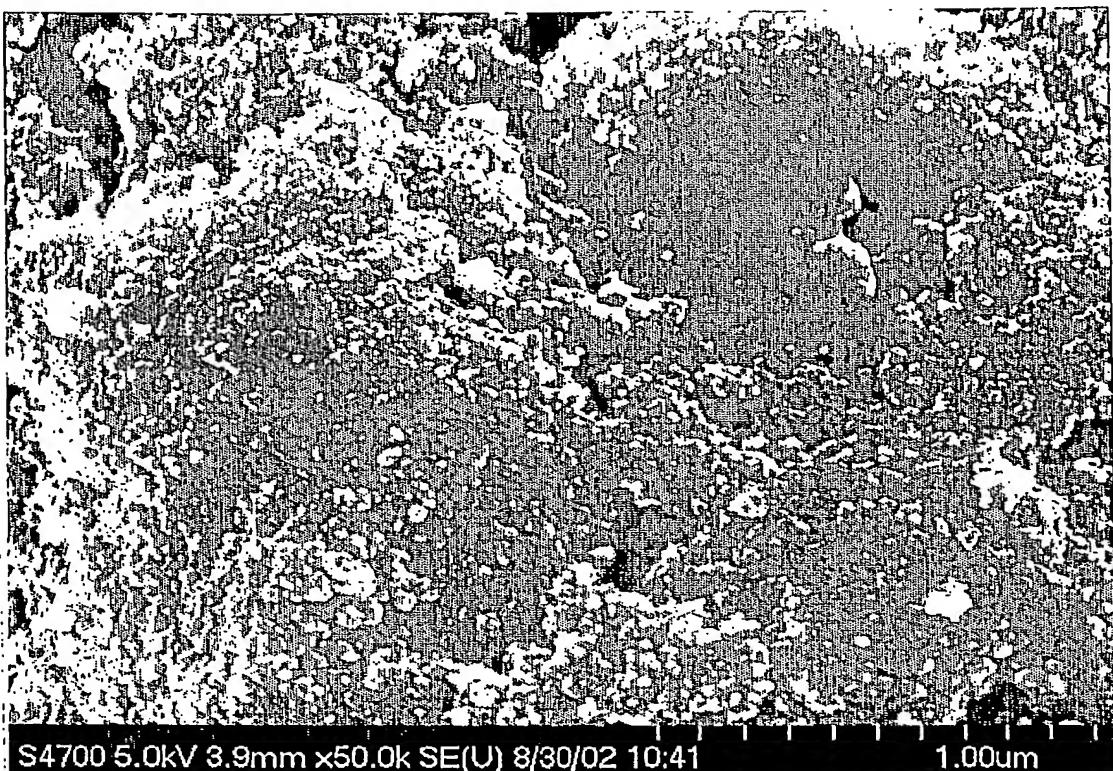
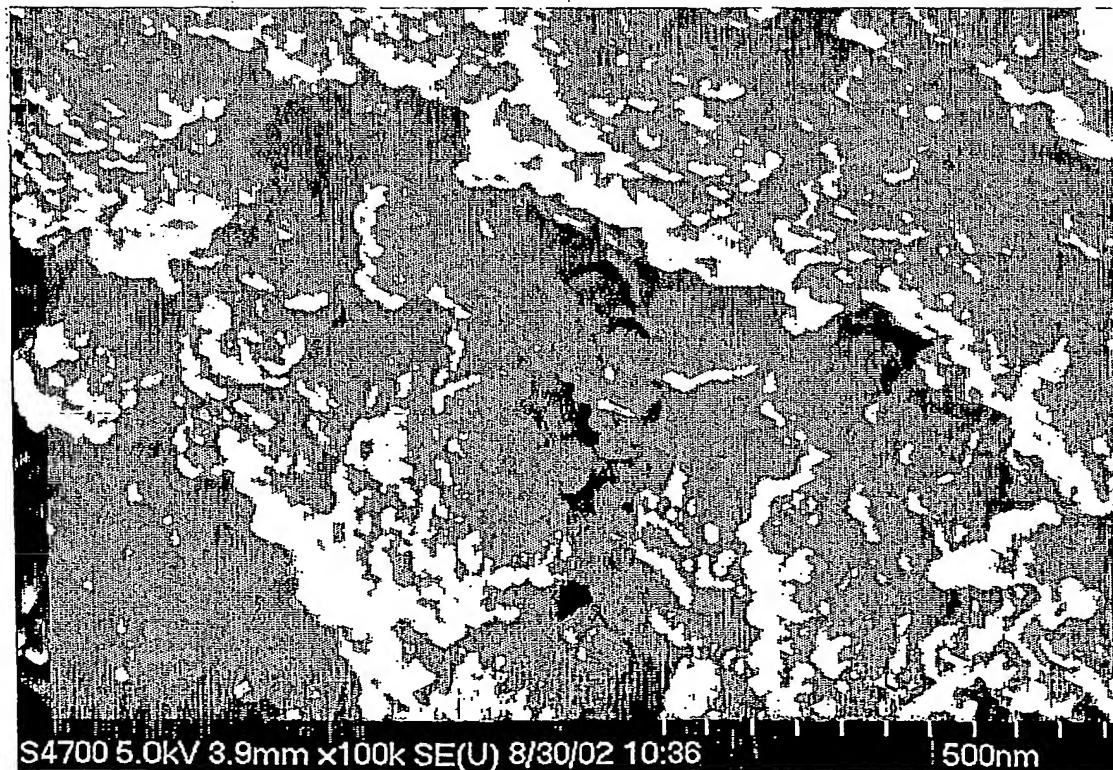
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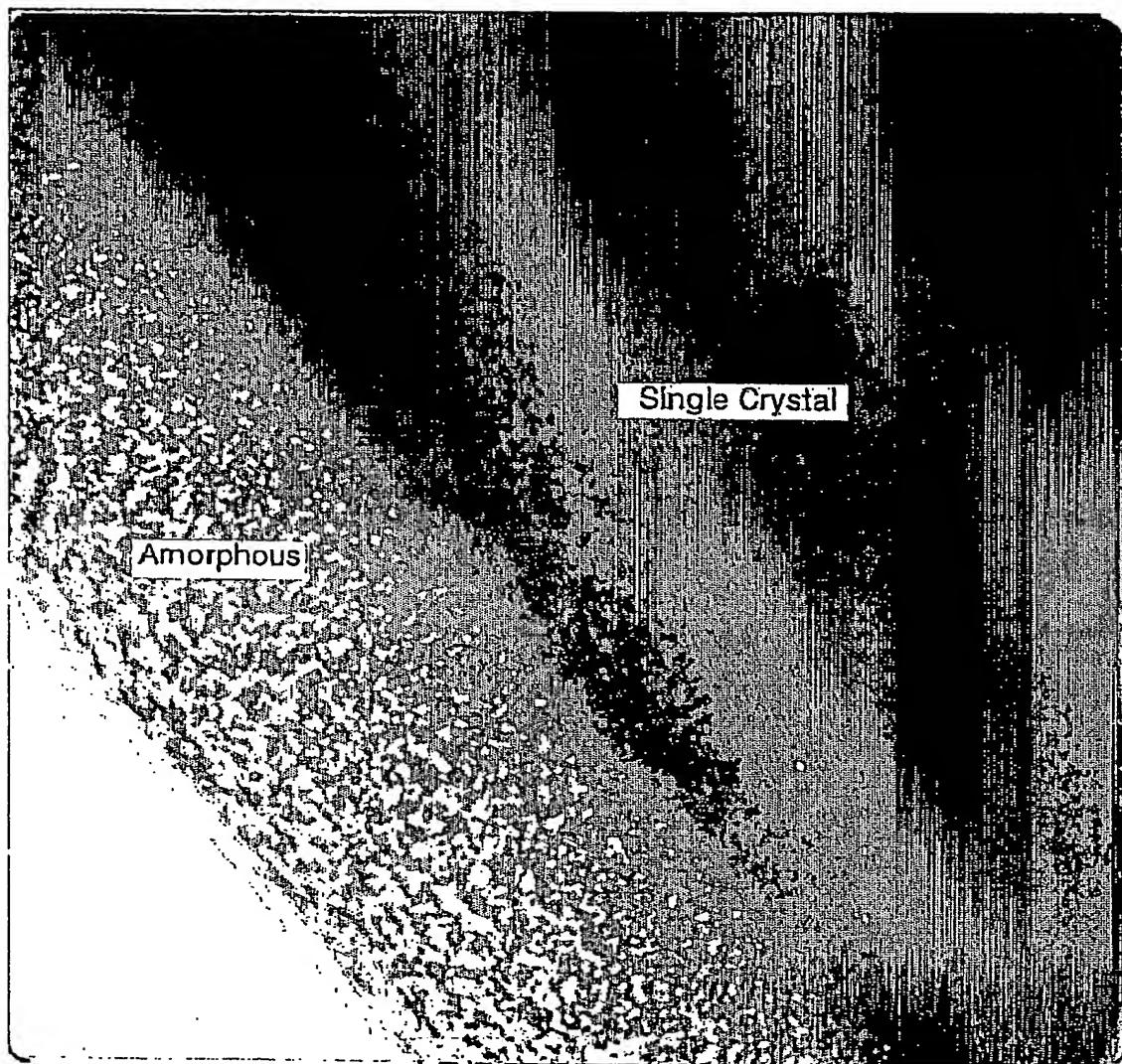


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~~FIG - 6A~~~~FIG - 6B~~**BEST AVAILABLE COPY**

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- (71) Applicant (*for all designated States except US*): HYDRO QUEBEC [CA/CA]; 75, Boulevard René-Lévesque Ouest, Montréal, Québec H2Z 1A4 (CA).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): MALEKI, Hossein [US/US]; 179 Hampton Hallow Dr., Lawrenceville, GE 30043 (US). SELMAN, Robert, J. [US/US]; 5532 S. Shore no.12E, Chicago, IL 60637 (US). GUERFI, Abdellab [CA/CA]; 8655 boul. Rivard, Brossard, Québec J4X 1W2 (CA). DUPUIS, Élisabeth [CA/CA]; 60 B rue St-François, McMasterville, Québec J3G 1E6 (CA). ZAGHIB, Karim [CA/CA]; 3672 Belcourt, Longueuil, Québec J4M 2M7 (CA).
- (74) Agent: OGILVY RENAULT; Suite 1600, 1981 McGill College Avenue, Montreal, Québec H3A 2Y3 (CA).
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WO 2003/049215 A3

(54) Title: CARBON-CARBON COMPOSITE PARTICLES, THEIR PREPARATION AND USE THEREFORE AS NEGATIVE ELECTRODE FOR LI-ION BATTERIES

(57) Abstract: A composite of particles of Carbon#1-Carbon#2, wherein Carbon#1 means a low crystallinity carbon and Carbon#2 means a high crystallinity carbon and the use of these particles in electrochemical systems, in sport equipments, in foundry industry and in the car and in aeronautic industries.

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/CA 02/01888

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 H01M4/58 C04B35/524 C04B35/628

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 977 292 A (MITSUI MINING CO LTD) 2 February 2000 (2000-02-02) paragraphs '0010!, '0014!, '0017!, '0019!, '0021!, '0022!, '0024!, '0043!, '0044!; claims 1,4,5; table 2	1,4-14, 17,19-24
X	US 5 908 715 A (LIU QINGGUO ET AL) 1 June 1999 (1999-06-01)  column 5, line 44 - line 66 claims 1-3; example 1	1,5,11, 17, 19-21, 23,24

Further documents are listed in the continuation of box C.

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Date of the actual completion of the International search

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/CA 02/01888

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 782 207 A (SHARP KK) 2 July 1997 (1997-07-02)  page 3, line 40 – line 42 page 3, line 49 – line 51 page 5, line 12 – line 14 -----	1-3,11, 17, 19-21,23
X	US 6 139 989 A (KAWAKUBO TAKAMASA ET AL) 31 October 2000 (2000-10-31) column 1, line 8 – line 13 column 3, line 14 – line 49 claims 1,3-6 -----	1,2,4,5, 24
P,X	US 2002/061445 A1 (HAYASHI MANABU ET AL) 23 May 2002 (2002-05-23) paragraphs '0012!, '0022!, '0024! – '0026!, '0029!, '0031!, '0033! – '0041!, '0043!, '0044!; claims 1,6 -----	1,11,24

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/CA 02/01888

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 0977292	A	02-02-2000	EP	0977292 A2		02-02-2000
			JP	3106129 B2		06-11-2000
			JP	2000106182 A		11-04-2000
			US	6432583 B1		13-08-2002
US 5908715	A	01-06-1999	NONE			
EP 0782207	A	02-07-1997	JP	3481063 B2		22-12-2003
			JP	9237638 A		09-09-1997
			DE	69609809 D1		21-09-2000
			DE	69609809 T2		18-01-2001
			EP	0782207 A1		02-07-1997
			US	6040092 A		21-03-2000
US 6139989	A	31-10-2000	JP	8227714 A		03-09-1996
US 2002061445	A1	23-05-2002	CN	1118880 B		20-08-2003
			EP	0917228 A1		19-05-1999
			ID	21480 A		17-06-1999
			WO	9854779 A1		03-12-1998
			JP	3193342 B2		30-07-2001
			JP	11054123 A		26-02-1999
			KR	2000029650 A		25-05-2000
			US	6403259 B1		11-06-2002